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(54) Polymers for cement dispersing admixtures

Polymer für zementdispergierende Zusatzmittel

Polymères pour compositions dispersantes pour ciment

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- Schober, Irene, Dr.
8008 Zürich (CH)
- Bürge, Theodor A.
8954 Geroldswil (CH)

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(74) Representative: Isler, Jörg
c/o Sika Technology AG
Intellectual Property Department
Tüffenwies 16
P.O. Box
8048 Zürich (CH)

(73) Proprietor: **Sika Schweiz AG**
8064 Zürich (CH)

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WO-A-97/03929 US-A- 5 707 445

(72) Inventors:
• Velten, Ulf, Dr.
5000 Aarau (CH)
• Sulser, Ueli
8102 Oberengstringen (CH)
• Widmer, Jürg, Dr.
8049 Zürich (CH)

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DescriptionBackground of the invention

5 [0001] On today's construction sites superplasticizers find wide spread use for improving concrete. In modern constructions in housing or civil engineering, which are heavy reinforced, prestressed or require high final strength and durability, concrete coming from ready mix plants or concrete which is mixed on job sites must fulfill sometimes extraordinary high requirements regarding water reduction, workability, compactation, durability and strength.

10 [0002] In former years, water reducers from mid to high range based on lignin, naphthalene sulfonic acid condensates, melamine formaldehyde condensates or copolymers based on maleic acids found intensive use. These water reducers were useful to reduce water content of fresh concrete and, thus, to enhance workability, fluidity ("slump"), durability and strength.

15 [0003] However, as from construction site the standards regarding properties of fresh and/or hardened concrete became more and more sophisticated, this kind of polymers were inappropriate if high water reduction was required, because this could only be achieved by adding high dosages of water reducer, which, however, led to undesired effects like strong retardation, stiffening and dramatically loss of fluidity (called "slump loss").

20 [0004] In recent years, a new kind of superplasticizers based on poly(acrylic acid) and polyethyleneglycol came up. Said superplasticizers were no longer linear polyelectrolyts but showed a comb like structure. Superplasticizers with this new structure caused a higher water reduction than the water reducers used before and were accompanied by a much lower retardation. Thus, this kind of new polymers was useful for modern construction sites with high standards because low dosages could be used with improved workability of fresh concrete and improved durability and final strength of hardened concrete.

[0005] Dispersants with the above mentioned features, obtained by copolymerizing (meth)acrylic acid or a salt thereof with (alkoxy)polyalkylene glycol mono(meth)acrylic ester are e.g. disclosed in EP 0 753 488.

25 [0006] Polymeric additives imparting to the wet cement composition the above mentioned advantages, and in addition comprising air detraining functional side chains, are disclosed in WO 97/00898.

30 [0007] However, despite of the improvement regarding water reduction and slump loss, it is still a challenge to fit to the various requirements coming from construction sites worldwide. This is due to different climates, cements, aggregates, cement replacing fillers etc., but also due to a wide spread application field like precast, ready mix, self compacting concrete, shotcrete, on site concrete etc., where the admixtures are faced some times with completely different demands.

35 [0008] Hence, to fit every request coming from construction sites, it is often necessary to use blends of polymers as water reducing admixtures. Consequently, a pool of differently performing polymers, i.e. polymers with high or moderate water reduction, with constant or increasing slump flow, with more or less retardation, or polymers with special features like set accelerating, and/or corrosion inhibiting must be available.

[0009] The polymer analogous reaction of carboxylic groups containing polymers with polyalkyleneglycol-monoalkylether, α -amino-polyalkyleneglycol- ω -alkylether or other amines is described in US-A-5728207, US-A-5840114 and WO-A-98/31643. However, the polymers disclosed in the above mentioned state of the art documents do not fit all various requests coming from construction sites worldwide.

40 [0010] Thus, it is desirable to provide improved polymers that are obtainable by an easy and convenient synthesis method, as well as such a method which gives the feasibility to establish a pool of differently performing polymers based on few raw materials and only one synthetical approach, but with different properties like high water reduction, constant slump flow or increasing slump flow.

45 Brief description of the drawings

[0011]

Figure 1 shows the kinetic behavior of the syntheses of polymer example E 4.

50 Figure 2 shows the hydrolysis of cleavable ester groups of polymer with (H1) and without (H2) reactant D-1.

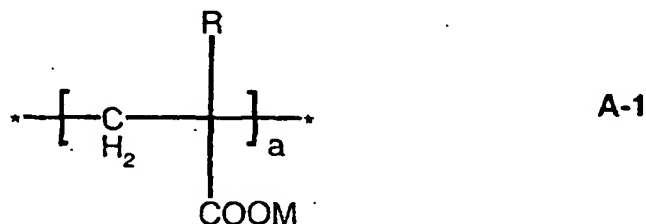
Brief description of the invention

55 [0012] Surprisingly, it has now been found that the reactions described in US-A-5728207, US-A-5840114 and WO-A-98/31643, can be improved such that it is suitable to synthesize a variety of polymers, with completely different properties, for e.g. precast, ready mix or for workability increasing applications, by varying the reaction time and improving the amount of amide/imide structures in said polymers obtainable by the inventive method.

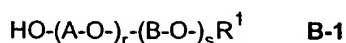
[0013] Thus, it was one object of the present invention to provide differently performing, modified poly(acrylates)

which are all obtainable by convenient synthesis and by one composition of reactants, whereby only the reaction time is varied. This method provides the feasibility to synthesize in a very convenient way differently performing polymers for precast, for readymix, or for slump keeping applications.

[0014] Said polymers according to the present invention are obtainable by reacting a poly(acrylic acid) A-1 with endgroups resulting from initiators and/or chain transfer agents that are inert for condensation reactions, said poly(acrylic acid) A-1 having a number average molecular weight of from 500 to 20'000

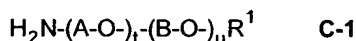


with o molar equivalents of a monofunctional polyalkyleneglycol-monoalkylether, represented by formula B-1



and optionally

with p molar equivalents of a monofunctional α -amino-polyalkyleneglycol- ω -alkylether, represented by formula C-1



and/or, optionally

with q molar equivalents of a primary or secondary amine, represented by formula D-1



wherein

R represents a hydrogen atom or a methyl group, or mixture thereof (wherever the term "or a mixture thereof" occurs in this specification in connection with the definition of substituents, it means that the compound of a specific formula can comprise several compounds of said formula only differing in the respective substituent);

M represents a hydrogen atom, a C₁ - C₅ - alkyl rest or an alkali metal, an alkaline earth metal or other two or three valent metal atoms, an ammonium or organic ammonium group (such as e.g. an alkyl and/or alkanol substituted ammonium group, in particular C₁ - C₄-alkyl and/or C₁ - C₄-alkanol substituted ammonium), or a mixture thereof; each R¹ independently from each other is a C₁ - C₄ alkyl rest, A and B represent alkylene groups with 2 - 4 C-atoms, the mixture of (A-O) and (B-O) may be formed by either random addition or block addition, and (A-O) \neq (B-O); R² and R³ independently from each other represent a hydrogen atom, or an aliphatic, cycloaliphatic, araliphatic or aromatic rest, or R² and R³ may together with the nitrogen atom to which they are bound form a morpholine or imidazole ring system, or another ring systems containing at least one hetero atom like nitrogen, sulfur or oxygen; or R² and R³ independently from each other represent oxyalkylene groups of the structure R⁵-(O-R⁶)_v-, wherein R⁵ represents a C₁ - C₄ alkyl rest and O-R⁶ represents an oxyalkylene group with 2 to 4 carbon atoms, whereby within the same structure R⁵-(O-R⁶)_v-, O-R⁶ can represent more than one kind of oxyalkylene group, wherein the mixture may be formed by either random addition or block addition;

wherein $a:o:p:q = 1:(0.1-0.95):(0-0.3):(0-0.3)$, preferably $a:o:p:q = 1:(0.1-0.95):(0-0.1):(0-0.1)$, more preferably $a:o:p:q = 1:(0.1-0.95):(0-0.05):(0-0.05)$, even more preferably $a:o:p:q = 1:(0.1-0.95):(0-0.02):(0-0.02)$, and most preferably $a:o:p:q = 1:(0.1-0.95):(0-0.01):(0-0.01)$, and

wherein $p + q < 0.3$, preferred $p + q < 0.1$, more preferred $p + q < 0.05$, even more preferred $p + q < 0.02$, and most preferred $p + q < 0.01$,
and

$$o + p + q \leq a;$$

r, s, t, u and v independently represent integers from 0 - 250;

$$r + s > 1;$$

$$t + u > 1;$$

at elevated temperatures, whereby the reaction can be stopped at different reaction times to get polymers with different properties, whereby said reaction times are determined dependent on the reaction kinetics influenced by the ratio of A-1, B-1 and optionally C-1 and/or D-1 and the temperature, whereby said reaction kinetics are determined by measuring the decrease of the acid number over the time, whereby said reaction is stopped,

I. at a high slope of decrease of the acid number over the time resulting in polymers with a high initial water reduction and a decreasing slump flow over the time
or

II. at a medium slope of decrease of the acid number over the time resulting in polymers with a high or medium initial water reduction and a constant slump flow over the time
or

III. at a small slope of decrease or no decrease of the acid number over the time resulting in polymers with a medium or low initial water reduction and an increasing slump flow over the time.

[0015] The determination of the kinetics of the reaction by measuring the decrease of the acid number over the time has of course not to be performed with any reaction but can be determined once and used for later reactions with the same characteristics.

[0016] In order to clearly distinguish Areas I, II, and III, it is furthermore advisable to determine for a specific composition of starting materials and reaction conditions the relevant properties of the polymer at different reaction times.

[0017] Where in the scope of the present invention high water reduction is mentioned, this means a water reduction of > 20%. Values between 10% and 20% are termed medium water reduction, and values below about 10% low water reduction.

[0018] In a preferred embodiment of the present invention, in the ratio $a:o:p:q$, $p + q \neq 0$, preferably $0 < p + q < 0.3$, more preferably $0 < p + q < 0.1$, even more preferably $0 < p + q < 0.05$, still more preferably $0 < p + q < 0.02$, and most preferably $0 < p + q < 0.01$, whereby in the case of $p + q \neq 0$ the lower limit is about 0.001.

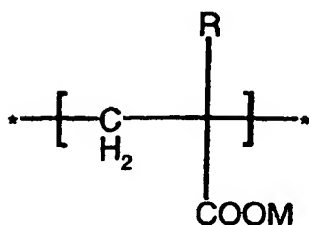
[0019] The present invention comprises a polymer in which 50 - 100 mole-% of the formula B-1 are represented by a structure in which A represents an alkylene group with 2 C-atoms and $s = 0$, or in which B represents an alkylene group with 2 C-atoms and $r = 0$, and in which O-R⁶ represents 50 - 100 mole-% of an oxyalkylene group with 2 C-atoms.

[0020] In a preferred polymer of the present invention, 50 - 100 mole-% of the formula C-1 are represented by a structure in which A represents an alkylene group with 2 C-atoms and $u = 0$, or in which B represents an alkylene group with 2 C-atoms and $t = 0$.

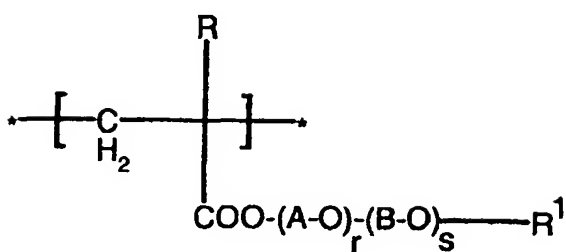
[0021] The modified acrylic polymers synthesized according to the present invention have dispersing, slump keeping or slump increasing properties, whereby the level of said properties can be determined by just varying the reaction time. They are composed of specific molar parts of at least two, preferably three or four constituent units selected from the group given by formulas A, B, C, and D, namely

m molar parts of

o molar parts of



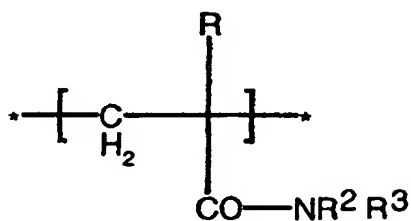
A



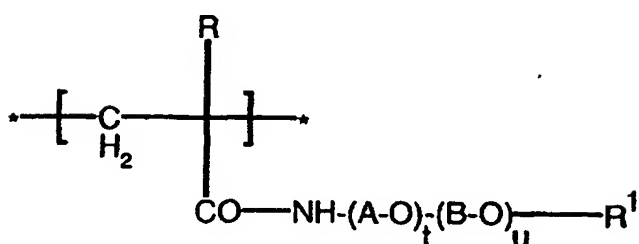
B

q molar parts of

p molar parts of



D



C

wherein

R represents a hydrogen atom or a methyl group, or a mixture thereof;

M represents a hydrogen atom, a C₁ - C₅ - alkyl rest or an alkali metal, an alkaline earth metal or other two or three valent metal atoms, an ammonium or organic ammonium group (such as e.g. an alkyl and/or alkanol substituted ammonium group, in particular C₁ - C₄-alkyl and/or C₁ - C₄-alkanol substituted ammonium), or a mixture thereof; each R¹ independently from each other is a C₁ - C₄ alkyl rest, A and B represent alkylene groups with 2 - 4 C-atoms, the mixture of (A-O) and (B-O) may be formed by either random addition or block addition, and (A-O) ≠ (B-O);

R² and R³ independently from each other represent a hydrogen atom, or an aliphatic, cycloaliphatic, araliphatic or aromatic rest, or R² and R³ may together with the nitrogen atom to which they are bound form a morpholine or imidazole ring system, or another ring systems containing at least one hetero atom like nitrogen, sulfur or oxygen; or R² and R³ independently from each other represent oxyalkylen groups of the structure R⁵-(O-R⁶)_v-, wherein R⁵ represents a C₁ - C₄ alkyl rest and O-R⁶ represents an oxyalkylene group with 2 to 4 carbon atoms, whereby within the same structure R⁵-(O-R⁶)_v-, O-R⁶ can represent more than one kind of oxyalkylene group, wherein the mixture may be formed by either random addition or block addition;

r, s, t, u and v independently represent integers from 0 - 250;

$$r + s > 1;$$

$$t + u > 1;$$

m, o, p, q are numerical values representing the molarity of the constituent units A, B, C and D present in the polymers, in a proportion of

m:o:p:q = (0.05-0.9):(0.05-0.95):(0-0.3):(0-0.3), preferred m:o:p:q = (0.05-0.9):(0.05-0.95):(0-0.1):(0-0.1), more preferred m:o:p:q = (0.05-0.9):(0.1-0.95):(0-0.05):(0-0.05), even more preferred m:o:p:q = (0.05-0.9):(0.1-0.95):(0-0.02):(0-0.02), and most preferred m:o:p:q = (0.05-0.9):(0.1-0.95):(0-0.01):(0-0.01), and wherein $p + q < 0.3$, preferred $p + q < 0.1$, more preferred $p + q < 0.05$, much more preferred $p + q < 0.02$, and most preferred $p + q < 0.01$, such, that $m + o + p + q = 1$.

[0022] In a preferred embodiment, in the ratio m:o:p:q, $p + q \neq 0$, preferably $0 < p + q < 0.3$, more preferably $0 < p + q < 0.1$, even more preferably $0 < p + q < 0.05$, still more preferably $0 < p + q < 0.2$, and most preferably $0 < p + q < 0.01$, whereby the lower limit of $p + q \neq 0$ preferably is about 0.001.

[0023] The present invention comprises a polymer in which 50 - 100 mole-% of the formula **B** are represented by a structure in which A represents an alkylene group with 2 C-atoms and $s=0$, or in which B represents an alkylene group with 2 C-atoms and $r=0$, and in which O-R⁶ represents 50 - 100 mole-% of an oxyalkylene group with 2 C-atoms.

[0024] In a preferred polymer 50 - 100 mole-% of the formula **C** are represented by a structure in which A represents an alkylene group with 2 C-atoms and $u=0$, or in which B represents an alkylene group with 2 C-atoms and $t=0$.

[0025] In another preferred embodiment, the modified acrylic polymers have a number average molecular weight of from 4000 to 100'000.

[0026] It was found, that the poly(acrylic acid) or its C₁-C₅-alkyl ester, or its salt has preferably a number average molecular weight of from 1'000 to 10'000. Furthermore, the poly(acrylic acid) must be synthesized in a way, that the endgroups of the poly(acrylic acid), which are resulting from initiators and/or chain transfer agents, are inert for reactions like acid catalyzed condensation reactions. This means, that the endgroups of one single modified acrylic polymer must not react with another single modified acrylic polymer in a way, which causes crosslinking.

[0027] The poly(acrylic acid) may be fully or partly neutralized before or after the polymer analogous reaction with an alkaline substance. Examples for this alkaline substance are metal hydroxides like alkali metal hydroxides and alkaline earth metal hydroxides, aluminum hydroxides or oxide hydroxides, tin or zinc compounds, ammonia, alkyl amines or hydroxyalkyl amines.

[0028] In the scope of the invention it was found that modified acrylic polymers are preferably obtained by reacting the components A-1, B-1 and/or, optionally C-1 and/or D-1 in the presence of sulfuric acid or p-toluene sulfonic acid as a catalyst and maintained at a temperature of about 140°C to 250°C, most preferred 150°C to 200°C.

[0029] Furthermore, it was found that in the polymer analogous condensation reaction according to this invention, the separation of water arising during the esterification, amidization or imidization, can be done either by blowing a gas stream over the reaction melt, or by applying a vacuum, or by using inert organic solvents as carrier. Suitable inert organic solvents are such solvents that give an azeotropic mixture with water and which have a boiling temperature of about 50°C to 300°C, preferably 80°C to 300°C, most preferably 100°C to 300°C. Inert organic solvents can support the polymer analogous condensation process at the beginning and/or during the reaction. Inert organic solvents can be aliphatic, cycloaliphatic, araliphatic or aromatic compounds, or mixtures thereof.

[0030] In other preferred embodiments reactant B-1 and C-1 independently from each other have a number average of weight of from 250 to 10'000.

[0031] Studying the kinetical behavior of the polymer analogous reaction towards modified poly(acrylate)s, it was surprisingly found that, depending on the reaction time, completely differently performing polymers can be achieved. Said synthesis for differently performing polymers that are suitable for use in dispersing admixtures is easily feasible using only one reactor and one favorite composition of reactants.

[0032] The kinetic behavior of the polymer analogous reaction of poly(acrylic acid)s A-1 with polyalkyleneglycol-monoalkylether B-1, α -amino-polyalkyleneglycol- ω -alkylether C-1 and primary or secondary amines D-1 can be monitored by determination of the acid number (mg KOH / g) over the time by taking samples at certain times.

[0033] Figure 1 represents the kinetical behavior of the syntheses of polymer example E 4, which shows a typical behavior for all syntheses:

[0034] Three different Areas I, II and III can be distinguished. Area I is characterized in that the slope of decrease of the acid number is high, Area II is characterized in that the slope of decrease of the acid number is medium and Area III is characterized in that the slope of decrease of the acid number is from low to no decrease. In particular, it was found, that one composition of reactants, which can be varied according to mentioned claims, results in polymers with completely different performance in concrete depending on the reaction time at a specific elevated temperature.

[0035] One specific embodiment of this invention are e.g. polymers obtainable according to Area I that show a high initial water reduction and are suitable for precast. Another specific embodiment are polymers obtainable according to Area II that show a high or medium initial water reduction and a constant slump flow over the time. Such polymers are suitable for readymix. Jet another embodiment are polymers synthesized according to Area III that show a medium or low initial water reduction and an increasing slump flow over the time. Such polymers are suitable for slump flow increasing applications. Properties of polymers according to Area I, II and III can be further adapted to specific needs by varying the composition of reactants.

[0036] Wherever here polymers obtainable according to a specific area or polymers according to a specific area are mentioned, this means polymers that are obtainable by stopping the reaction in one of the Areas I, II, or III.

[0037] The slump increasing effect of modified poly(acrylic acid)s according to Area III is due to the hydrolysis of cleavable ester groups under cementitious conditions, whereby the most important condition is a high pH value. It was found, that the hydrolysis behavior of cleavable side groups of the inventive polymers can be influenced and controlled in an easy way by adapting the composition of the reactants in the polymers, most preferably by variation of reactants C-1 and/or D-1.

[0038] The hydrolysis kinetics can be determined by adding NaOH to a solution of modified poly(acrylic acid) and monitoring the cleavage of the ester groups by using a pH-indicator. Figure 2 shows inventive polymers with reactant D-1 and without reactant D-1, which show a significantly different hydrolyzation behavior.

[0039] Summarized, the presence of reactants C-1 and/or D-1, namely the presence of amid or imid structure in the inventive modified poly(acrylic acid), makes it possible, to take significant influence on the kinetic cleavage behavior of cleavable side groups. This is due to side group effects of the amide or imide structure to cleavable ester groups.

[0040] Hence, it is a specific aspect of this invention, that variation of at least one of the reactants B-1, C-1 and D-1, more preferred a variation of reactants C-1 and D-1 influence the hydrolysis kinetics of the cleavable side groups. At least some of the above mentioned properties of the polymers synthesized according to Area I, Area II or Area III can be influenced and so enhanced, that preferred polymers with long shelf lifes, and preferred polymers with special slump increasing properties are achieved.

Detailed description of the invention

[0041] The invention is based of extensive studies of modified poly(acrylic acid)s having polyalkyleneglycol side chains, which are connected to the poly(acrylic acid) backbone via ester, amide or imide bonds, and, optionally, which include amide or imide structures based on primary or secondary amines.

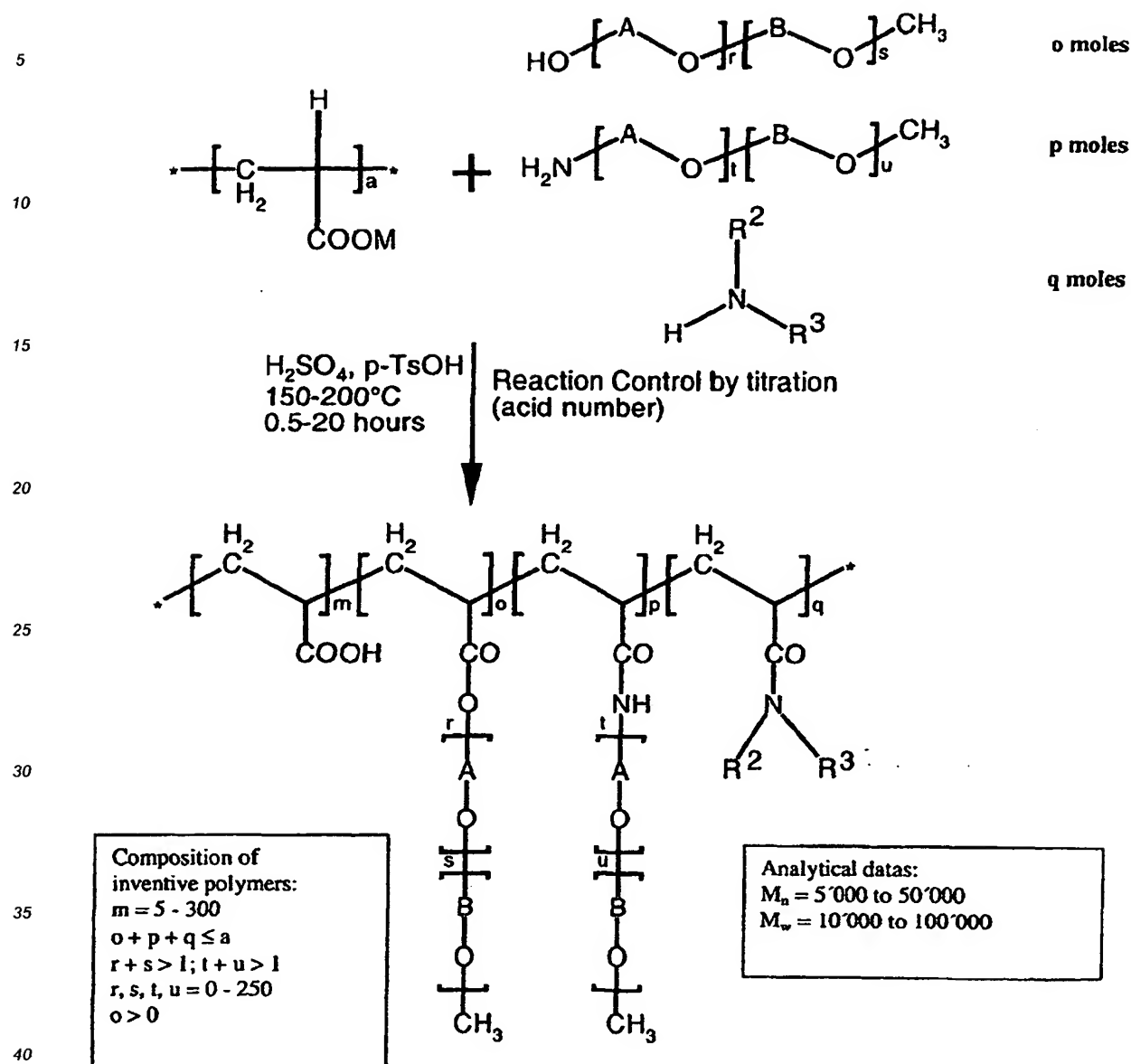
[0042] In particular, the synthesis of the modified poly(acrylic acid)s, i.e. the kinetics of the synthesis, has intensively been studied in order to achieve polymers that are differently performing in concrete, and that are obtainable based on one composition of reactants only by varying the reaction time. Due to distinction of the polymer analogous condensation into three Areas I, II and III three differently performing polymers based on one composition of reactants can be achieved. In concrete, polymers according to Area I show suitability for precast due to high water reduction. In concrete, polymers according to Area II show suitability for readymix due to high water reduction and good slump life, and polymers according to Area III show suitability for slump increasing properties.

[0043] Furthermore, it was found that amines used to modify poly(acrylic acid)s influence the hydrolysis kinetics of cleavable groups in the investigated polymers, and that therefore special properties of polymers according to Area I, II and III can be obtained by varying the ratio of reactants A-1, B-1, C-1 and D-1.

[0044] The preparation of the inventive modified poly(acrylic acid)s according to Area I, II and III was carried out as described in the reaction scheme below:

Reaction Scheme - Preferred synthesis of the inventive polymers

[0045] 1 mol of a poly(acrylic acid) of a molecular weight of 1000 to 10'000 is reacted at elevated temperature with o moles polyalkyleneglycol-monoalkylether, p moles of an α -amino-polyalkyleneglycol- ω -alkylether and q moles of a primary or secondary amine in presence of an acid catalyst:



[0046] After the end of the reaction, which is detected by the current acid number, the resulting modified poly(acrylic acid)s are received as a melt which solidifies at lower temperatures to an amorphous mass. The modified poly(acrylic acid)s obtainable according to the preceding synthesis can be handled either as solid, as melt, because remelting is easily feasible, or as diluted solution, because either solid or molten modified poly(acrylic acid)s according to this invention are soluble in water to any amounts. The polymer can be stored, transported and applied as a melt, as a solid, or as a solution.

[0047] The polymers of this invention are employed either as dispersing agents, in particular polymers according Area I and II, or the inventive polymers, in particular polymers according to Area III, can be used as slump flow increasing agents, to overcome the problem of drop of slump flow over the time.

[0048] In a preferred embodiment, the polymers can be used for water reducing applications as single polymers or as mixtures of said inventive polymers according to Area I, II and III. Polymers according to Area III are most preferably used in admixtures as polymer blends. In another preferred embodiment, modified acrylic polymers according to this invention can also be blended with other dispersing admixtures, preferably admixtures selected from the group consisting of sulfonated melamine condensates, sulfonated naphthalene condensates, lignosulfonates, substituted male-

amid-vinyl-copolymers and acrylic or methacrylic copolymers with polyalkylene side chains, or mixtures thereof.

[0049] Modified acrylic polymers according to this invention, or admixtures comprising same preferably furthermore contain at least one defoaming or antifoaming agent and/or at least one air controlling agent.

[0050] A further aspect of the present invention is a mortar, concrete, cement or cementitious binder containing the modified acrylic polymer according to the present invention in an amount of 0.01 to 10% by weight of the binder, said mortar or concrete having a unit content of binder composition of cement or a mixture of cement and latent hydraulic binder and/or inert microscopic powder of 100 to 800 kg/m³, preferably of 250 to 650 kg/m³.

[0051] In a preferred embodiment, the cement is selected from the group consisting of Portland cement, white cement, high alumina cement or blended cement, and the latent hydraulic or inert microscopic powder is selected from the group consisting of fly ash, slag, natural pozzolane, silica fume, burnt oil shale, metakaolin or calcium carbonate, or mixtures thereof.

[0052] The cement composition of the present invention may further comprise conventional admixtures like plasticizers, superplasticizers, air entraining admixtures, defoamers, retarders, set accelerators, hardening accelerators, hydrophobizing or shrinkage reducing admixtures or corrosion inhibitors.

[0053] Still a further embodiment of this invention is an aqueous slurry of microscopic powders containing the modified acrylic polymers according to this invention, or a mixture thereof, in an amount of 0.01 to 10% by weight of the binder. Most preferred is, that the microscopic powder is calcium carbonate, gypsum or gypsum based.

[0054] The inventive admixture could be used in liquid form or as a powder form and could be added before, during or after the grinding operation of the cement or the cementitious binder.

Examples

[0055] In the following examples, the synthesis of the inventive polymers usable in admixtures for dispersing and/or slump increasing properties that are also an object of the present invention is explained in more detail by means of the examples E1 - E16, H1 - H2 and the mixtures of different example polymers M1 - M6. All polymer solutions were adjusted to 40% solid content.

[0056] In test example 1 polymers are synthesized according to the Areas I, II and III and their different properties were tested in mortar. In test example 2 blends of polymers synthesized according to the Areas I and III were tested in mortar. In test example 3 the influence of reactants C-1 or D-1 to the kinetic behavior of cleavage ester side groups is demonstrated.

[0057] Polymers E1, E5, E9 and E13 are synthesized according Area I, polymers E2, E3, E6, E7, E10, E11, E14 and E15 are synthesized according Area II and polymers E4, E8, E12 and E16 are synthesized according Area III. The number average molecular weight of the inventive polymers was determined by size exclusion chromatography using polyethyleneglycol standards considering only the polymer peak.

Example E1 to E4 (Polymer E1 to E4)

[0058] 160 g of an aqueous solution of a partly neutralized 4000 molecular weight poly(acrylic acid) and 7.5 g 50 wt. % sulfuric acid were placed in a glass reactor fitted with a thermometer, stirrer, a gas inlet tube and a distillation assembly. The solution was heated to 70°C and 360 g of a 1000 number average molecular weight polyethyleneglycol-monomethylether and 30 g of a 1000 number average molecular weight α -amino-polyethyleneglycol- ω -methylether were added.

[0059] The mixture was heated up under a steady stream of nitrogen and kept at 165°C. After 2 h (E1), 4h (E2), 6h (E3) and 8h (E4) stirring at 165°C samples were taken. Each sample was cooled down to 90°C and, finally, water was added to obtain a 40 wt.-% solution.

Table 1:

Polymer examples E1-4				
Example No.	Reaction time (h)	Final acid number (mg KOH/g)	M _n	Polymer content of resulting aq. solution
E1	2	78.6	10400	40 ± 1
E2	4	67.9	11300	40 ± 1
E3	6	62.3	13600	40 ± 1
E4	8	57.8	13100	40 ± 1

Example E5 to E8 (Polymer E5 to E8)

[0060] 160 g of an aqueous solution of a partly neutralized 4000 molecular weight poly(acrylic acid) and 7.5 g 50 wt. % sulfuric acid were placed in a glass reactor fitted with a thermometer, stirrer, a gas inlet tube and a distillation assembly. The solution was heated to 70°C and 360 g of a 1000 number average molecular weight polyethyleneglycol-monomethylether and 6.48 g of 3-(2-methoxyethoxy)-propyl-amin were added.

[0061] The mixture was heated up under a steady stream of nitrogen and kept at 165°C. After 2 h (E5), 4h (E6), 6h (E7) and 8h (E8) stirring at 165°C samples were taken. Each sample was cooled down to 90°C and, finally, water was added to obtain a 40 wt.-% solution.

Table 2:

Polymer examples E5-8				
Example No.	Reaction time (h)	Final acid number (mg KOH/g)	M _n	Polymer content of resulting aq. solution
E5	2	79.7	9700	40 ± 1
E6	4	66.8	11100	40 ± 1
E7	6	59.5	12100	40 ± 1
E8	8	54.4	13000	40 ± 1

Example E9 to E12 (Polymer E9 to E12)

[0062] 160 g of an aqueous solution of a partly neutralized 4000 molecular weight poly(acrylic acid) and 7.5 g 50 wt. % sulfuric acid were placed in a glass reactor fitted with a thermometer, stirrer, a gas inlet tube and a distillation assembly. The solution was heated to 70°C and 400 g of a 1000 number average molecular weight polyethyleneglycol-monomethylether was added.

[0063] The mixture was heated up under a steady stream of nitrogen and kept at 165°C. After 2 h (E9), 4h (E10), 6h (E11) and 8h (E12) stirring at 165°C samples were taken. Each sample was cooled down to 90°C and, finally, water was added to obtain a 40 wt.-% solution.

Table 3:

Polymer examples E9-12				
Example No.	Reaction time (h)	Final acid number (mg KOH/g)	M _n	Polymer content of resulting aq. solution
E9	2	75.7	11100	40 ± 1
E10	4	69	11500	40 ± 1
E11	6	56.7	13500	40 ± 1
E12	8	56.5	13400	40 ± 1

Example E13 to E16 (Polymer E13 to E16)

[0064] 160 g of an aqueous solution of a partly neutralized 4000 molecular weight poly(acrylic acid) and 7.5 g 50 wt. % sulfuric acid were placed in a glass reactor fitted with a thermometer, stirrer, a gas inlet tube and a distillation assembly. The solution was heated to 70°C and 360 g of a 1000 number average molecular weight polyethyleneglycol-monomethylether and 4.2 g of 1,4-Oxazinan were added.

[0065] The mixture was heated up under a steady stream of nitrogen and kept at 165°C. After 2 h (E13), 4h (E14), 6h (E15) and 8h (E16) stirring at 165°C samples were taken. Each sample was cooled down to 90°C and, finally, water was added to obtain a 40 wt.-% solution.

Table 4:

Polymer examples E13-16				
Example No.	Reaction time (h)	Final acid number (mg KOH/g)	M _n	Polymer content of resulting aq. solution
E13	2	74.6	10200	40 ± 1
E14	4	68.5	11200	40 ± 1
E15	6	59.5	11600	40 ± 1
E16	8	58.4	15500	40 ± 1

Example H1 (Polymer H1)

[0066] 160 g of an aqueous solution of a partly neutralized 4000 molecular weight poly(acrylic acid) and 7.5 g 50 wt. % sulfuric acid were placed in a glass reactor fitted with a thermometer, stirrer, a gas inlet tube and a distillation assembly. The solution was heated to 70°C and 360 g of a 1000 number average molecular weight polyethyleneglycol-monomethylether and 12 g dicyclohexylamine were added.

[0067] The mixture was heated up under a steady stream of nitrogen and kept at 165°C. After 2 h stirring at 165°C the acid number achieved a value of 62.8 and the mixture was cooled down. At 90°C 667 g of water was added to obtain a 40%-solution.

Example H2 (Polymer H2)

[0068] 160 g of an aqueous solution of a partly neutralized 4000 molecular weight poly(acrylic acid) and 7.5 g 50 wt. % sulfuric acid were placed in a glass reactor fitted with a thermometer, stirrer, a gas inlet tube and a distillation assembly. The solution was heated to 70°C and 395 g of a 1000 number average molecular weight polyethyleneglycol-monomethylether were added.

[0069] The mixture was heated up under a steady stream of nitrogen and kept at 165°C. After 2 h stirring at 165°C the acid number achieved a value of 62.8 and the mixture was cooled down. At 90°C 702 g of water was added to obtain a 40%-solution.

Table 5:

Polymer examples H1 - H2					
Example No.	Reaction time (h)	Final acid number (mg KOH/g)	M _n	Polymer content of resulting aq. solution	Cleavable ester groups in mmol/g polymer
H1	2	62.8	10600	40 ± 1	0.7925
H2	2	62.8	10600	40 ± 1	0.845

Test examples

[0070] The test examples 1 and 2 were performed to demonstrate the properties of the polymers synthesized according to Area I, II and III, namely polymers with fluidizing effects (Area I and II) and polymers with slump flow increasing properties (Area III). The inventive polymers were tested in mortar, in admixtures as individual polymers (Area I, II and III) and as polymer blends (Area I and III).

[0071] Test example 3 shows the influence of amides according to reactants C-1 and D-1 on the kinetic behavior of the hydrolyzation of the cleavable ester groups.

Test Example 1

[0072] The workability of concrete or mortar dependent on the use of one or more of the inventive polymers and comparative polymers was tested. The consistency of freshly prepared mortar, i.e. the mobility and viscosity, is the most important characteristic of workability. The consistency of freshly prepared mortar was investigated as mortar shows good correlation to concrete.

Table 6:

Composition of the fresh mortar mixtures	
Components	Quantity in kg
Normal Portland Cement, Type 1. (EU 197-1)	1.0
lime stone filler	0.2
sand 0 to 1.2 mm*	1.267
sand 1.2 to 4 mm*	1.067
sand 4 to 8 mm*	1.667
Total water (mixing water and water of the copolymer solution)	0.42
Inventive polymers or comparative polymer, g solid	0.004

* washed and dried

[0073] The filler, sand and cement were blended in a Hobart type mortar mixer for 60 seconds then the water containing the admixtures was added and the mortar mechanically kneaded for 3 minutes.

[0074] The consistency was determined by using a "flow table spread" test according to DIN 18555, part 2. The diameters of the spread mortar was measured in two directions and the average value was regarded as flow value. The measurement was repeated after 30 and 60 minutes with 30 seconds mixing of the mortar. The change of the flow value with time is a measure for the loss of fluidity of the mortar.

[0075] For the freshly prepared mortar, the fluidizing effect is dependent on the dosage of the superplasticizer. Usually, from 0.2 to 1.5 % solid matter quantities (in dissolved form), referred to the weight of cement, are added. To a high degree, the effect is also dependent on the chemical structure and the molecular weight of the polymer, which is forming the basis of the fluidizer. In particular, in this invention the reaction time according to the Areas I, II and III shows a significant influence on the fluidizing effect of the inventive polymers.

[0076] In order to demonstrate increased effectiveness of the inventive copolymers, the flow behavior of mortar mixtures containing polymers E1 to E16 were measured as mentioned.

Table 7:

Mortar tests of example polymers E1 - E16								
Test Mixture No	Polymer example	Dosage in % of cement weight *	Flow table spread in mm , x minutes after mixing			Compressive strength in Newton/mm ² , y days after mixing		% -Air content of fresh mix
			x = 0	30	60	y = 1	7	
1	E1	0.83	219	186	144	26.3	51.4	2.9
2	E2	0.83	205	211	191	25.1	46.3	2.4
3	E3	0.83	176	211	205	25.3	47.1	3.0
4	E4	0.83	146	194	211	25.1	48	4.1
5	E5	0.83	212	175	135	27.2	46.6	3.4
6	E6	0.83	220	214	214	25.9	48.3	6.8
7	E7	0.83	141	184	173	26.1	48.7	3.2
8	E8	0.83	134	188	208	28.0	48.5	3.5
9	E9	0.9	232	226	202	23.7	47.2	11
10	E10	0.9	206	232	247	23.4	49.6	6.0
11	E11	0.9	176	242	234	21.9	44.8	7.4

* all polymers are defoamed with 0.2 % triisobutyl phosphate

Table 7: (continued)

Mortar tests of example polymers E1 - E16								
Test Mixture No	Polymer example	Dosage in % of cement weight *	Flow table spread in mm , x minutes after mixing			Compressive strength in Newton/mm ² , y days after mixing		%Air content of fresh mix
			x = 0	30	60	y = 1	7	
12	E12	0.9	175	237	232	23.9	49.7	4.8
13	E13	0.9	252	235	226	19.7	45.1	6.0
14	E14	0.9	238	243	236	21.7	48.5	4.5
15	E15	0.9	185	241	238	22.3	49.6	5.8
16	E16	0.9	156	239	237	21.5	47.6	4.9

* all polymers are defoamed with 0.2 % triisobutyl phosphate

Test example 2

[0077] Test example 2 shows the effectiveness of blends of inventive polymers according to Area I and III. Different ratios of inventive polymers were used in the polymer blends. All tests were carried out as mentioned in Test example 1.

Table 8:

Mortar tests of example polymers E1, E4 and E5, E8 and blends thereof										
Test Mixture No	Polymer example	Polymers mixed	Ratio of polymer mix	Dosage in % of cement weight	Flow table spread in mm , x minutes after mixing			Compressive strength in Newton/mm ² , y days after mixing		%Air content after mix
					x = 0	30	60	y = 1	7	
17	E1	-	-	0.9	252	244	225	26.3	51.4	5.7
18	M1	E1/E4	1/3	0.9	197	247	250	24.4	46.6	4.4
19	M2	E1/E4	1/1	0.9	236	240	234	24.4	49.0	3.8
20	M3	E1/E4	3/1	0.9	247	245	232	26.0	49.9	4.8
21	E4	-	-	0.9	179	234	239	25.1	48.0	5.5
22	E5	-	-	0.9	246	212	174	27.2	46.6	6.0
23	M4	E5/E8	1/3	0.9	177	246	227	25.8	46.7	4.7
24	M5	E5/E8	1/1	0.9	209	234	229	26.0	49.7	4.2
25	M6	E5/E8	3/1	0.9	230	223	193	26.6	45.4	4.6
26	E8	-	-	0.9	157	225	223	28.0	48.5	5.4

* all polymers and polymer blends are defoamed with 0.2 % triisobutyl phosphate

Test example 3

[0078] Test example 3 was performed to demonstrate the influence of amid/imide structures to the hydrolysis behavior of cleavable ester groups in the modified poly(acrylic acid)s of this invention. Therefore, the pH value was adapted to a comparable value as concrete, i.e. 12 - 14. Under this alkaline conditions cleavable ester groups will hydrolyze, which can be detected by back titration with diluted HCl solution and a pH indicator.

[0079] The procedure was performed as followed: In a flask 50 g of a 40 wt-% of modified poly(acrylic acid) of this invention, 50 g pure water and 30 droplets of a 1 wt.-% phenolphthalein solution were mixed at room temperature. Afterwards, the solution was neutralized with 1 N aqueous NaOH solution. Under stirring 100 g of an 0.1 N aqueous NaOH solution was added so that the solution became red. The flask was closed to avoid evaporation.

[0080] At certain times a sample consisting of 20 g of the solution was taken and 0.1 N HCl was added dropwise until the solutions became colorless. Table 9 shows the results of this experiment.

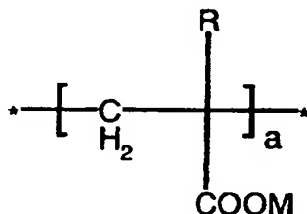
Table 9:

Hydrolysis of cleavable ester groups of polymer with (H1) and without (H2) reactant D-1				
Time (h)	Polymer H1, consumed 0.1 N HCl solution	Polymer H2, consumed 0.1 N HCl solution	Polymer H1, percentage of cleaved ester groups	Polymer H2, percentage of cleaved ester groups
1.0	0.1	1.5	0.8	11.7
2.5	0.3	1.8	2.1	13.7
3.5	0.8	1.9	6.7	14.5
4.0	0.8	2.1	6.7	16.0
5.0	0.9	2.2	7.5	16.8
8.0	1.1	2.5	8.8	19.2
12.0	1.3	2.8	10.5	21.9
20.0	1.6	3.4	13.4	26.2
40.0	2.1	3.9	17.2	30.5
66.0	2.3	4.4	19.3	34.0

Claims

1. A process for producing a modified acrylic polymer comprising reacting

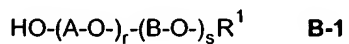
(A) a poly(acrylic acid) with endgroups resulting from initiators and/or chain transfer agents that are inert for condensation reactions, said poly(acrylic acid) A-1 having a molecular weight of from 500 to 20'000



A-1

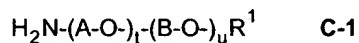
and

(B) o molar parts of a monofunctional polyalkyleneglycolmonoalkylether B-1



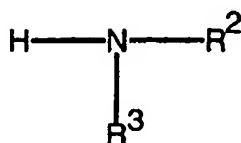
and optionally

(C) p molar parts of a monofunctional α -aminopolyalkyleneglycol- ω -alkylether C-1



and optionally

(D) q molar parts primary or secondary amine D-1



D-1

wherein

R represents a hydrogen atom or a methyl group, or a mixture thereof;

M represents a hydrogen atom, a $\text{C}_1 - \text{C}_5$ alkyl rest or an alkali metal, an alkaline earth metal or other two or three valent metal atoms, an ammonium or organic ammonium group, or a mixture thereof;

each R^1 independently from each other is a $\text{C}_1 - \text{C}_4$ alkyl rest, A and B represent alkylene groups with 2 - 4 C-atoms, the mixture of (A-O) and (B-O) may be formed by either random addition or block addition, and (A-O) \neq (B-O);

whereby 50 - 100 mole-% of B-1 are represented by a structure in which A represents an alkylene group with 2 C-atoms and $s=0$, or in which B represents an alkylene group with 2 C-atoms and $r=0$, and

R^2 and R^3 independently from each other represent a hydrogen atom, or an aliphatic, cycloaliphatic, araliphatic or aromatic rest, or R^2 and R^3 may together with the nitrogen atom to which they are bound form a morpholine or imidazole ring system, or another ring systems containing at least one hetero atom like nitrogen, sulfur or oxygen; or R^2 and R^3 independently from each other represent oxyalkylene groups of the structure $\text{R}^5-(\text{O}-\text{R}^6)_v$ -, wherein R^5 represents a $\text{C}_1 - \text{C}_4$ alkyl rest and $\text{O}-\text{R}^6$ represents an oxyalkylene group with 2 to 4 carbon atoms, whereby within the same structure $\text{R}^5-(\text{O}-\text{R}^6)_v$ -, $\text{O}-\text{R}^6$ can represent more than one kind of oxyalkylene group, wherein the mixture may be formed by either random addition or block addition;

whereby $\text{O}-\text{R}^6$ comprises 50 - 100 mole-% of an oxyalkylene group with 2 C-atoms, in a molar ratio of

$a:o:p:q = 1:(0.1-0.95):(0-(<0.3)):(0-(<0.3))$, and

wherein $p + q < 0.3$, and

$$o + p + q \leq a;$$

r, s, t, u and v independently represent integers from 0 - 250;

$$r + s > 1;$$

$$t + u > 1;$$

in the presence of a catalyst at elevated temperatures following a certain kinetic influenced by the ratio of A-1, B-1 and, optionally C-1 and optionally D-1 and temperature, in which the reaction can be followed by the decrease of the acid number over the time, in which the reaction can be stopped at different reaction times resulting into polymers with different properties, said reaction is stopped

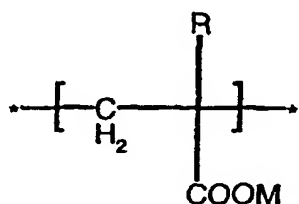
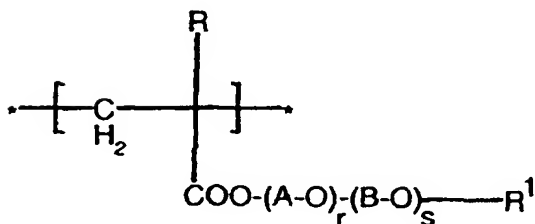
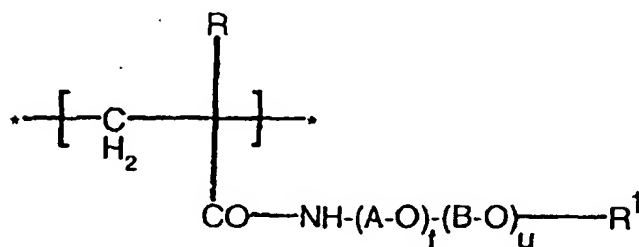
I. at a high slope of decrease of the acid number over the time resulting into polymers with a high initial water reduction of $>20\%$ and a decreasing slump flow over the time
or

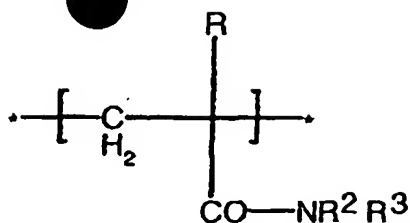
II. at a medium slope of decrease of the acid number over the time resulting into polymers with a high or medium initial water reduction of at least 10% and a constant slump flow over the time
or

III. at a small slope of decrease or no decrease of the acid number over the time resulting into polymers with

a medium or low water reduction of at most 20 % and an increased slump flow over the time.

2. The modified acrylic polymer of claim 1 wherein 50 - 100 mole-% of the formula **C-1** are represented by a structure in which A represents an alkylene group with 2 C-atoms and $u=0$, or in which B represents an alkylene group with 2 C-atoms and $t=0$.
3. The modified acrylic polymer of claim 1 or 2, wherein $p + q \neq 0$.
4. The modified acrylic polymer of anyone of claims 1 to 3, wherein $a:o:p:q = 1:(0.1-0.95):(0-(< 0.1)):(0-(< 0.1))$, and wherein $p + q < 0.1$.
5. The modified acrylic polymer of anyone of claims 1 to 3, wherein $a:o:p:q = 1:(0.1-0.95):(0-(< 0.02)):(0-(< 0.02))$, and wherein $p + q < 0.02$.
6. The modified acrylic polymer of anyone of claims 1 to 3, wherein $a:o:p:q = 1:(0.1-0.95):(0-(< 0.01)):(0-(< 0.01))$, and wherein $p + q < 0.01$.
7. The modified acrylic polymer of anyone of the preceding claims, wherein the lower limit of $p + q$ is about 0.001.
8. A modified acrylic polymer, obtainable by the process as defined in anyone of the preceding claims which is composed of m molar units of the group given by formula **A** below, o molar units of the group given by formula **B** below, optionally p molar units of the group given by formula **C** below, and optionally q molar units of the group given by formula **D** below, whereby:

**A****B****C**



wherein

R, M, R¹, A, B, (A-O), (B-O), R², R³, R⁵, O-R⁶, r, s, t, u, v, r + s, and t + u are as defined in claim 1;

whereby 50 - 100 mole-% of B are represented by a structure in which A represents an alkylene group with 2 C-atoms and s=0, or in which B represents an alkylene group with 2 C-atoms and r=0, and wherein

m, o, p, q are numerical values representing the molarity of the constituent units A, B, C and D present in the polymers, in a proportion of

m:o:p:q = (0.05-0.9):(0.1-0.95):(0-(<0.3)):(0-(<0.3)),

and wherein p + q < 0.3,

such, that m + o + p + q = 1.

9. The modified acrylic polymer of claim 8, wherein 50 - 100 mole-% of the formula C are represented by a structure in which A represents an alkylene group with 2 C-atoms and u=0, or in which B represents an alkylene group with 2 C-atoms and t=0.

10. The modified acrylic polymer of claim 8 or 9, wherein p + q \neq 0.

11. The modified acrylic polymer of anyone of claims 8 to 10, wherein m:o:p:q = (0.05-0.9):(0.1-0.95):(0-(<0.1)):(0-(<0.1)), and wherein p + q < 0.1.

12. The modified acrylic polymer of anyone of claims 8 to 10, wherein m:o:p:q = (0.05-0.9):(0.1-0.95):(0-(<0.20)):(0-(<0.02)), and wherein p + q < 0.02.

13. The modified acrylic polymer of anyone of claims 8 to 10, wherein m:o:p:q = (0.05-0.9):(0.1-0.95):(0-(<0.01)):(0-(<0.01)), and wherein p + q < 0.01.

14. The modified acrylic polymer of anyone of claims 8 to 13, wherein the lower limit of p + q is about 0.001.

15. The modified acrylic polymer according to claims 8 to 14, **characterized in that** the number average molecular weight is from 4000 to 100'000.

16. The modified acrylic polymer according to claims 8 to 14, **characterized in that** it is obtainable by a synthesis wherein the reactant A-1 has a number average molecular weight of from 1000 to 10'000.

17. The modified acrylic polymer according to claims 8 to 16, **characterized in that** it is obtainable by a synthesis wherein the reactant B-1 has a number average molecular weight of from 250 to 10'000 and the reactant C-1 has a number average molecular weight of from 250 to 10'000.

18. The modified acrylic polymer according to claims 8 to 17, **characterized in that** it is obtainable by reacting reactants A-1 and B-1, and optionally C-1 and optionally D-1 in the presence of an acid catalyst.

19. The modified acrylic polymer according to claims 8 to 17, **characterized in that** it is obtainable by a synthesis that is carried out using inert organic solvents as carrier.

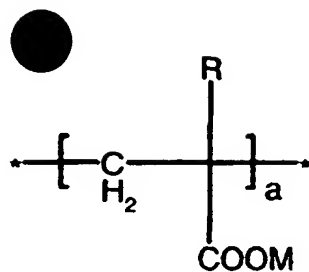
20. The modified acrylic polymer according to claims 8 to 19, obtainable by using reactants A-1 and B-1, and optionally C-1 and optionally D-1, whereby the reaction was stopped at a high slope of the decrease of the acid number over

the time resulting in a polymer with a high initial water reduction of >20 % and a decreasing slump flow over the time, which can be used especially for precast applications.

21. The modified acrylic polymer according to 8 to 19, obtainable by using reactants A-1 and B-1, and optionally C-1 and/or D-1, whereby the reaction was stopped at a medium slope of the decrease of the acid number over the time resulting in a polymer with a high or medium initial water reduction of at least 10 % and a constant slump flow over the time, which can be used especially for readymix applications.
22. The modified acrylic polymer according to claims 8 to 19, obtainable by using reactants A-1 and B-1, and optionally C-1 and/or D-1, whereby the reaction was stopped at a small slope of the decrease of the acid number over the time to linear behavior resulting in a polymer with a medium or low initial water reduction of at most 20 % and an increasing slump flow over the time, which can be used especially for slump flow increasing applications.
23. An admixture in liquid or solid form comprising at least one modified acrylic polymer according to claims 8 to 22.
24. An admixture in liquid or solid form comprising at least one modified acrylic polymer according to claims 20 to 22.
25. The admixture of claim 23 or 24, **characterized in that** it comprises at least two modified acrylic polymers in various ratios resulting in an admixture with high water reduction and constant slump flow over the time.
26. The admixture of anyone of claims 23 to 25 furthermore comprising further dispersing agents selected from the group consisting of sulfonated melamine condensates, sulfonated naphthalene condensates, lignosulfonates, substituted maleamid-vinyl-copolymers and acrylic or methacrylic copolymers with polyalkyleneglycol side chains, and mixtures thereof.
27. A mortar, concrete, cement or cementitious binder, containing at least one modified acrylic polymer according to claims 8 to 22 in an amount of 0.01 to 10% by weight of the binder, said mortar or concrete having a unit content of binder composition of 100 to 800 kg/m³ whereby said binder composition is selected from the group consisting of a cement, a mixture of cement, a latent hydraulic powder, a mixture of latent hydraulic powders, and mixtures thereof optionally together with one or more inert microscopic powder(s).
28. The mortar, concrete, cement or cementitious binder according to claim 27, **characterized in that** the cement is selected from the group consisting of Portland cement, white cement, high alumina cement, blended cement, and mixtures thereof, and the latent hydraulic or inert microscopic powder is selected from the group consisting of fly ash, slag, natural pozzolane, silica fume, burnt oil shale, metakaolin calcium carbonate, and mixtures thereof.
29. The mortar, concrete, cement or cementitious binder according to claim 27 or 28, **characterized in that** the admixture in liquid or powder form containing the modified acrylic polymers is added before, during or after the grinding operation of the cement or the cementitious binder.
30. An aqueous slurry of microscopic powder containing a modified acrylic polymer according to claims 8 to 22, or a mixture thereof, in an amount of 0.01 to 10% by weight of the binder.
31. The aqueous slurry of microscopic powder according to claim 30, **characterized in that** the microscopic powder is calcium carbonate, gypsum or gypsum based.

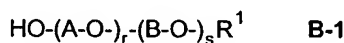
Patentansprüche

1. Verfahren für das Herstellen eines modifizierten Acrylpolymer, umfassend das Umsetzen von
 - (A) einer Polyacrylsäure mit Endgruppen, die aus Initiatoren und/oder Kettenübertragungsmitteln stammen, die inert für Kondensationsreaktionen sind, wobei die Polyacrylsäure A-1 ein Molekulargewicht von 500 bis 20.000 aufweist

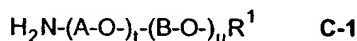
**A-1**

und

(B) o molaren Teilen eines monofunktionellen Polyalkylenglykolmonoalkylethers B-1

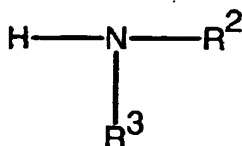


und gegebenenfalls

(C) p molaren Teilen eines monofunktionellen α -Amino-polyalkylenglykol- ω -alkylethers C-1

und gegebenenfalls

(D) q molaren Teilen eines primären oder sekundären Amins D-1

**D-1**

wobei

R ein Wasserstoffatom oder eine Methylgruppe oder eine Mischung derselben darstellt;

M ein Wasserstoffatom, einen C₁-C₅-Alkylrest oder ein Alkalimetall, ein Erdalkalimetall oder andere zwei- oder dreiwertige Metallatome, eine Ammonium- oder eine organische Ammoniumgruppe oder eine Mischung derselben bedeutet;jedes R¹ unabhängig voneinander ein C₁-C₄-Alkylrest ist, A und B Alkylengruppen mit 2 - 4 C-Atomen bedeuten, die Mischung aus (A-O) und (B-O) entweder durch Zufallsaddition oder Blockaddition gebildet werden kann und (A-O) \neq (B-O) ist;

wobei 50 - 100 Mol-% an **B-1** durch eine Struktur dargestellt werden, in welcher A eine Alkylengruppe mit 2 C-Atomen und s=0 bedeutet oder in welcher B eine Alkylengruppe mit 2 C-Atomen und r=0 bedeutet, und R² und R³ unabhängig voneinander ein Wasserstoffatom oder einen aliphatischen, cycloaliphatischen, araliphatischen oder aromatischen Rest bedeuten oder R² und R³ zusammen mit dem Stickstoffatom, an welches sie gebunden sind, ein Morpholin- oder Imidazol-Ringsystem oder ein anderes Ringsystem bilden können, welches mindestens ein Heteroatom wie Stickstoff, Schwefel oder Sauerstoff enthält; oder R² und R³ unabhängig voneinander Oxyalkylengruppen der Struktur R⁵-(O-R⁶)_v- darstellen, wobei R⁵ einen C₁-C₄-Alkylrest darstellt und O-R⁶ eine Oxyalkylengruppe mit 2 bis 4 Kohlenstoffatomen darstellt, wobei innerhalb der gleichen Struktur R⁵-(O-R⁶)_v-, O-R⁶ mehr als eine Art von Oxyalkylengruppe darstellen kann, wobei die Mischung entweder durch Zufallsaddition

oder durch Blockaddition gebildet werden kann;
 wobei O-R⁶ 50 - 100 Mol-% einer Oxyalkylengruppe mit 2 C-Atomen umfasst,
 in einem molaren Verhältnis von
 a:o:p:q = 1:(0,1-0,95):(0-($<0,3$)):(0-($<0,3$)), und
 wobei p + q < 0,3 und

$$o + p + q \leq a;$$

r, s, t, u und v unabhängig voneinander ganze Zahlen von 0 - 250 darstellen;

$$r + s > 1;$$

$$t + u > 1;$$

in Gegenwart eines Katalysators bei erhöhter Temperatur gemäß einer bestimmten Kinetik, die beeinflusst wird durch das Verhältnis von A-1, B-1 und gegebenenfalls C-1 und gegebenenfalls D-1 und die Temperatur, wobei die Reaktion durch die Abnahme der Säurezahl über die Zeit mitverfolgt werden kann, wobei die Reaktion nach verschiedenen Reaktionszeiten gestoppt werden kann, was zu Polymeren mit verschiedenen Eigenschaften führt, die Reaktion gestoppt wird

I. bei einer starken Neigung der Abnahme der Säurezahl mit der Zeit, was zu Polymeren mit einer hohen anfänglichen Verflüssigung von >20 % und einem mit der Zeit abnehmenden Ausbreitmaß führt, oder

II. bei einer mittleren Neigung der Abnahme der Säurezahl mit der Zeit, was zu Polymeren mit einer hohen oder mittleren anfänglichen Verflüssigung von mindestens 10 % und einem über die Zeit konstanten Ausbreitmaß führt, oder

III. bei einer geringen Neigung der Abnahme oder keiner Abnahme der Säurezahl mit der Zeit, was zu Polymeren mit einer mittleren oder geringen anfänglichen Verflüssigung von höchstens 20 % und einem über die Zeit zunehmenden Ausbreitmaß führt.

2. Modifiziertes Acrylpolymer gemäß Anspruch 1, bei dem 50 - 100 Mol-% der Formel C-1 durch eine Struktur dargestellt sind, bei der A eine Alkylengruppe mit 2 C-Atomen darstellt und u = 0 ist oder bei der B eine Alkylengruppe mit 2 C-Atomen darstellt und t = 0 ist.

3. Modifiziertes Acrylpolymer gemäß Anspruch 1 oder 2, bei dem p + q \neq 0 ist.

4. Modifiziertes Acrylpolymer gemäß einem der Ansprüche 1 bis 3, bei dem a:o:p:q = 1:(0,1-0,95):(0-($<0,1$)):(0-($<0,1$)) und p + q < 0,1 ist.

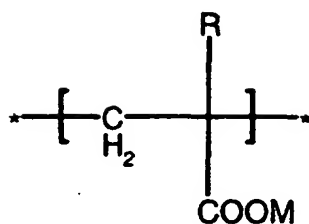
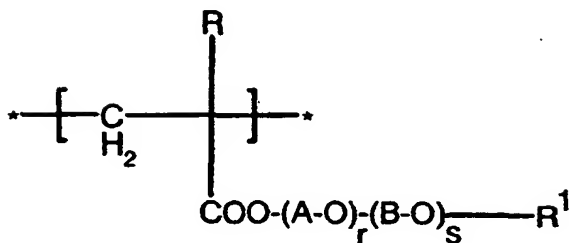
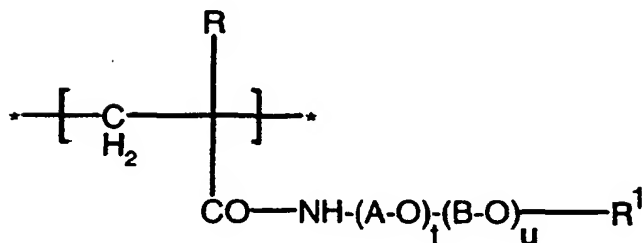
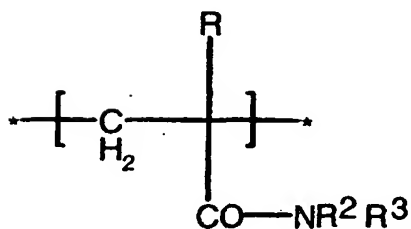
5. Modifiziertes Acrylpolymer gemäß einem der Ansprüche 1 bis 3, bei dem a:o:p:q = 1:(0,1-0,95):(0-($<0,02$)):(0-($<0,02$)) und p + q < 0,02 ist.

6. Modifiziertes Acrylpolymer gemäß einem der Ansprüche 1 bis 3, bei dem a:o:p:q = 1:(0,1-0,95):(0-($<0,01$)):(0-($<0,01$)) und p + q < 0,01 ist.

7. Modifiziertes Acrylpolymer gemäß einem der vorhergehenden Ansprüche, bei dem die untere Grenze von p + q ca. 0,001 beträgt.

8. Modifiziertes Acrylpolymer, das erhältlich ist durch das in einem der vorhergehenden Ansprüche definierte Verfahren und zusammengesetzt ist aus m molaren Einheiten der durch Formel A unten angegebenen Gruppe, o molaren Einheiten der durch Formel B unten angegebenen Gruppe, gegebenenfalls p molaren Einheiten der durch Formel C unten angegebenen Gruppe und gegebenenfalls q molaren Einheiten der durch Formel D unten ange-

gegebenen Gruppe, wobei

ABCD

wobei

R, M, R¹, A, B, (A-O), (B-O), R², R³, R⁵, O-R⁶, r, s, t, u, v, r + s und t + u wie in Anspruch 1 definiert sind:

wobei 50 - 100 Mol-% von B durch eine Struktur dargestellt werden, in der A eine Alkylengruppe mit 2 C-Atomen und s=0 bedeutet oder in welcher B eine Alkylengruppe mit 2 C-Atomen und r=0 bedeutet,

m, o, p, q numerische Werte sind, welche die Molarität der Bestandteil-Einheiten A, B, C und D in den Polymeren darstellen, in einem Verhältnis von

m:o:p:q = (0,05-0,9):(0,1-0,95):(0-($<0,3$)):(0-($<0,3$))

und wobei p + q $< 0,3$,

derart, dass $m + o + p = 1$.

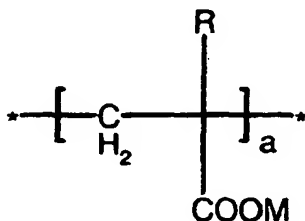
9. Modifiziertes Acrylpolymer gemäß Anspruch 8, wobei 50 - 100 Mol-% der Formel C durch eine Struktur dargestellt werden, in der A eine Alkylengruppe mit 2 C-Atomen und $u = 0$ bedeutet oder in welcher B eine Alkylengruppe mit 2 C-Atomen und $t = 0$ bedeutet.
10. Modifiziertes Acrylpolymer gemäß Anspruch 8 oder 9, bei dem $p + q \neq 0$ ist.
11. Modifiziertes Acrylpolymer gemäß einem der Ansprüche 8 bis 10, bei dem $m:o:p:q = (0,05-0,9):(0,1 - 0,95):(0-<0,1):(0-<0,1)$ und $p + q < 0,1$ ist.
12. Modifiziertes Acrylpolymer gemäß einem der Ansprüche 8 bis 10, bei dem $m:o:p:q = (0,05-0,9):(0,1-0,95):(0-<0,02):(0-<0,02)$ und $p + q < 0,02$ ist.
13. Modifiziertes Acrylpolymer gemäß einem der Ansprüche 8 bis 10, bei dem $m:o:p:q = (0,05-0,9):(0,1-0,95):(0-<0,01):(0-<0,01)$ und $p + q < 0,01$ ist.
14. Modifiziertes Acrylpolymer gemäß einem der Ansprüche 8 bis 13, bei dem die untere Grenze von $p + q$ ca. 0,001 beträgt.
15. Modifiziertes Acrylpolymer gemäß den Ansprüchen 8 bis 14, **dadurch gekennzeichnet, dass** das zahlengemittelte Molekulargewicht von 4.000 bis 100.000 beträgt.
16. Modifiziertes Acrylpolymer gemäß den Ansprüchen 8 bis 14, **dadurch gekennzeichnet, dass** es erhältlich ist mittels einer Synthese, in welcher das Reaktionsmittel A-1 ein zahlengemitteltes Molekulargewicht von 1.000 bis 10.000 hat.
17. Modifiziertes Acrylpolymer gemäß den Ansprüchen 8 bis 16, **dadurch gekennzeichnet, dass** es erhältlich ist mittels einer Synthese, in welcher das Reaktionsmittel B-1 ein zahlengemitteltes Molekulargewicht von 250 bis 10.000 aufweist und das Reaktionsmittel C-1 ein zahlengemitteltes Molekulargewicht von 250 bis 10.000 hat.
18. Modifiziertes Acrylpolymer gemäß den Ansprüchen 8 bis 17, **dadurch gekennzeichnet, dass** es erhältlich ist durch Umsetzen der Reaktionsmittel A-1 und B-1 und gegebenenfalls C-1 und gegebenenfalls D-1 in Gegenwart eines Säurekatalysators.
19. Modifiziertes Acrylpolymer gemäß den Ansprüchen 8 bis 17, **dadurch gekennzeichnet, dass** es erhältlich ist durch eine Synthese, die ausgeführt wird unter Verwendung inerter organischer Lösungsmittel als Träger.
20. Modifiziertes Acrylpolymer gemäß den Ansprüchen 8 bis 19, das erhältlich ist unter Verwendung der Reaktionsmittel A-1 und B-1 und gegebenenfalls C-1 und gegebenenfalls D-1, wobei die Reaktion bei einer starken Neigung der Abnahme der Säurezahl mit der Zeit gestoppt wurde, was in einem Polymer mit hoher anfänglicher Verflüssigung von >20% und einem mit der Zeit abnehmenden Ausbreitmaß resultiert, welches insbesondere für Fertigteilanwendungen verwendet werden kann.
21. Modifiziertes Acrylpolymer gemäß den Ansprüchen 8 bis 19, das erhältlich ist unter Verwendung der Reaktionsmittel A-1 und B-1 und gegebenenfalls C-1 und/oder D-1, wobei die Reaktion bei einer mittleren Neigung der Abnahme der Säurezahl mit der Zeit gestoppt wurde, was in einem Polymer mit hoher oder mittlerer anfänglicher Verflüssigung von mindestens 10% und einem über die Zeit konstanten Ausbreitmaß resultiert, welches insbesondere für Fertigmischungs-Anwendungen eingesetzt werden kann.
22. Modifiziertes Acrylpolymer gemäß den Ansprüchen 8 bis 19, das erhältlich ist unter Verwendung der Reaktionsmittel A-1 und B-1 und gegebenenfalls C-1 und/oder D-1, wobei die Reaktion bei einer geringen Neigung der Abnahme der Säurezahl mit der Zeit bis zu linearem Verhalten gestoppt wurde, was in einem Polymer mit mittlerer oder geringer anfänglicher Verflüssigung von höchstens 20% und einem mit der Zeit zunehmendem Ausbreitmaß resultiert, welches insbesondere für Anwendungen zur Zunahme des Ausbreitmaßes eingesetzt werden kann.
23. Zusatzmittel in flüssiger oder fester Form, umfassend mindestens ein modifiziertes Acrylpolymer gemäß den Ansprüchen 8 bis 22.

24. Zusatzmittel in flüssiger oder fester Form, umfassend mindestens ein modifiziertes Acrylpolymer gemäß den Ansprüchen 20 bis 22.
25. Zusatzmittel gemäß Anspruch 23 oder 24, **dadurch gekennzeichnet, dass** es mindestens zwei modifizierte Acrylpolymere in verschiedenen Verhältnissen umfasst, was in einem Zusatzmittel mit hoher Verflüssigung und konstantem Ausbreitmaß über die Zeit resultiert.
26. Zusatzmittel gemäß einem der Ansprüche 23 bis 25, welches zusätzlich weitere Dispergiermittel, ausgewählt aus der Gruppe bestehend aus sulfonierten Melaminkondensaten, sulfonierten Naphthalinkondensaten, Lignosulfonaten, substituierten Maleamid-Vinyl-Copolymeren und Acryl- oder Methacrylcopolymeren mit Polyalkylenglykol-Seitenketten und Mischungen derselben umfasst.
27. Mörtel, Beton, Zement oder zementöses Bindemittel, umfassend mindestens ein modifiziertes Acrylpolymer gemäß den Ansprüchen 8 bis 22 in einer Menge von 0,01 bis 10 Gew.-%, bezogen auf das Bindemittel, wobei der Mörtel oder Beton einen Einheitsgehalt an Bindemittelzusammensetzung von 100 bis 800 kg/m³ besitzt, wobei die Bindemittelzusammensetzung ausgewählt ist aus der Gruppe bestehend aus einem Zement, einer Mischung aus Zement, einem latent hydraulischen Pulver, einer Mischung aus latent hydraulischen Pulvern und Mischungen derselben, gegebenenfalls zusammen mit einem oder mehreren inerten mikroskopischen Pulvern.
28. Mörtel, Beton, Zement oder zementöses Bindemittel gemäß Anspruch 27, **dadurch gekennzeichnet, dass** der Zement ausgewählt ist aus der Gruppe bestehend aus Portlandzement, Weißzement, Tonerdezement, gemischtem Zement und Mischungen derselben und dass das latent hydraulische Bindemittel oder inerte mikroskopische Pulver ausgewählt ist aus der Gruppe bestehend aus Flugasche, Schlacke, natürlichem Pozzolan, Silicafume, gebranntem Ölschiefer, Metakaolincalciumcarbonat und Mischungen derselben.
29. Mörtel, Beton, Zement oder zementöses Bindemittel gemäß Anspruch 27 oder 28, **dadurch gekennzeichnet, dass** das Zusatzmittel in flüssiger oder Pulverform, welches die modifizierten Acrylpolymere umfasst, vor, während oder nach dem Mahlvorgang des Zementes oder des zementösen Bindemittels zugegeben wird.
30. Wässrige Aufschlämmung von mikroskopischem Pulver, die ein modifiziertes Acrylpolymer gemäß den Ansprüchen 8 bis 22 oder eine Mischung derselben in einer Menge von 0,01 bis 10 Gew.-%, bezogen auf das Bindemittel, enthält.
31. Wässrige Aufschlämmung von mikroskopischem Pulver gemäß Anspruch 30, **dadurch gekennzeichnet, dass** das mikroskopische Pulver Calciumcarbonat, Gips oder auf Gips basierend ist.

Revendications

1. Procédé de production d'un polymère acrylique modifié comprenant la réaction

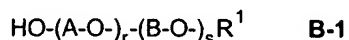
(A) d'un poly(acide acrylique) avec des groupes terminaux résultant d'initiateurs et/ou d'agents de transfert de chaîne inertes vis-à-vis des réactions de condensation, ledit poly(acide acrylique) A-1 présentant un poids moléculaire de 500 à 20 000



A-1

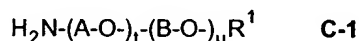
et

(B) de o parties molaires d'un monoalkyléther de polyalkylèneglycol monofonctionnel B-1



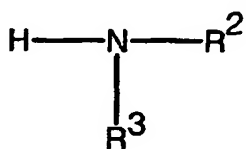
et éventuellement

(C) de p parties molaires d'un ω-alkyléther d'un α-aminopolyalkylèneglycol monofonctionnel C-1



et éventuellement

(D) de q parties molaires d'une amine primaire ou secondaire D-1



D-1

où

R représente un atome d'hydrogène ou un groupe méthyle, ou leurs mélanges;

M représente un atome d'hydrogène, un radical alkyle en C₁-C₅ ou un métal alcalin, un métal alcalino-terreux ou d'autres atomes métalliques bivalents ou trivalents, un groupe ammonium ou ammonium organique, ou leurs mélanges;

chaque R¹ représente indépendamment des autres un radical alkyle en C₁-C₄, A et B représentent des groupes alkylène comportant de 2 à 4 atomes de carbone, le mélange de (A-O) et (B-O) peut être formé par addition statistique ou addition par blocs, et (A-O) ≠ (B-O);

où 50 à 100% molaires de B-1 sont représentés par une structure dans laquelle A représente un groupe alkylène comportant 2 atomes de carbone et s = 0, ou bien dans laquelle B représente un groupe alkylène comportant 2 atomes de carbone et r = 0, et

R² et R³ représentent indépendamment l'un de l'autre un atome d'hydrogène, ou un radical aliphatique, cycloaliphatique, araliphatique ou aromatique, ou bien R² et R³ peuvent former ensemble avec l'atome d'azote auquel ils sont liés un système de noyau de morpholine ou d'imidazole, ou un autre système de noyau contenant au moins un hétéroatome comme l'azote, le soufre ou l'oxygène; ou bien R² et R³ représentent indépendamment l'un de l'autre des groupes oxyalkylène de structure R⁵-(O-R⁶)_v-, où R⁵ représente un radical alkyle en C₁-C₄ et O-R⁶ représente un groupe oxyalkylène comportant de 2 à 4 atomes de carbone, où dans une même structure R⁵-(O-R⁶)_v-, -O-R⁶ peut représenter plus d'un type de groupe oxyalkylène, le mélange pouvant être formé par addition statistique ou addition par blocs;

où O-R⁶ comprend de 50 à 100% molaires d'un groupe oxyalkylène à 2 atomes de carbone, en proportion molaire de

a:o:p:q = 1:(0,1-0,95):(0-(<0,3)):(0-(<0,3)), et

où

$$p + q < 0,3,$$

et

$$o + p + q \leq a;$$

r, s, t, u et v représentent indépendamment les uns des autres des nombres entiers de 0 à 250;

$$r + s > 1;$$

$$t + u > 1;$$

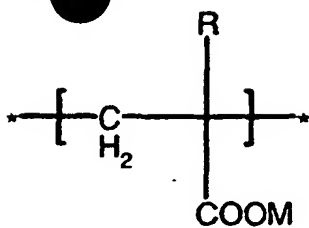
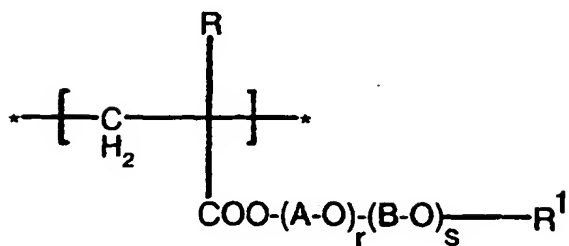
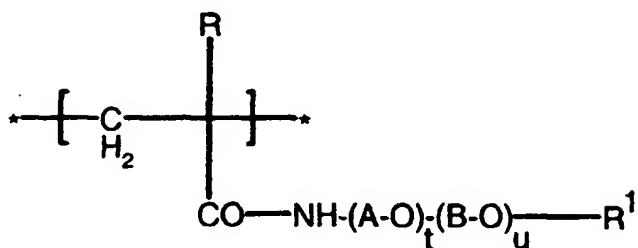
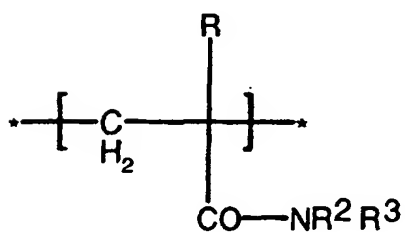
en présence d'un catalyseur et à haute température, selon une certaine cinétique influencée par le rapport entre A-1, B-1 et éventuellement C-1 et éventuellement D-1 et par la température, la réaction pouvant être suivie par la baisse de l'indice d'acide en fonction du temps, où la réaction peut être arrêtée à différentes durées de réaction pour donner des polymères de propriétés différentes, ladite réaction étant arrêtée

I. à une forte pente de la baisse de l'indice d'acide en fonction du temps, pour donner des polymères à réduction d'eau initiale élevée de plus de 20% et à affaissement décroissant en fonction du temps
ou

II. à une pente moyenne de la baisse de l'indice d'acide en fonction du temps, pour donner des polymères à réduction d'eau initiale élevée ou moyenne d'au moins 10% et à affaissement constant en fonction du temps
ou

III. à une pente faible ou nulle de la baisse de l'indice d'acide en fonction du temps, pour donner des polymères à réduction d'eau initiale moyenne ou faible d'au plus 20% et à affaissement croissant en fonction du temps.

2. Polymère acrylique modifié selon la revendication 1, dans lequel 50 - 100% molaires de la formule C-1 sont représentés par une structure dans laquelle A représente un groupe alkylène comportant 2 atomes de carbone et u = 0 ou dans laquelle B représente un groupe alkylène comportant 2 atomes de carbone et t = 0.
3. Polymère acrylique modifié selon la revendication 1 ou 2, dans lequel $p + q \neq 0$.
4. Polymère acrylique modifié selon l'une quelconque des revendications 1 à 3, dans lequel $a:o:p:q = 1:(0,1-0,95):(0-(<0,1)):(0-(<0,1))$ et dans lequel $p + q < 0,1$.
5. Polymère acrylique modifié selon l'une quelconque des revendications 1 à 3, dans lequel $a:o:p:q = 1:(0,1-0,95):(0-(<0,02)):(0-(<0,02))$ et dans lequel $p + q < 0,02$.
6. Polymère acrylique modifié selon l'une quelconque des revendications 1 à 3, dans lequel $a:o:p:q = 1:(0,1-0,95):(0-(<0,01)):(0-(<0,01))$ et dans lequel $p + q < 0,01$.
7. Polymère acrylique modifié selon l'une quelconque des revendications précédentes, dans lequel la limite inférieure de $p + q$ est d'environ 0,001.
8. Polymère acrylique modifié, susceptible d'être obtenu par le procédé défini dans l'une quelconque des revendications précédentes, composé de m unités molaires du groupe illustré par la formule A ci-dessous, de o unités molaires du groupe illustré par la formule B ci-dessous, éventuellement de p unités molaires du groupe illustré par la formule C ci-dessous, et éventuellement de q unités molaires du groupe illustré par la formule D ci-dessous,

ABCD

où

R, M, R¹, A, B, (A-O), (B-O), R², R³, R⁵, O-R⁶, r, s, t, u, v, r + s et t + u sont tels que définis dans la revendication 1;

où 50 à 100% molaires de B sont représentés par une structure dans laquelle A représente un groupe alkylène comportant 2 atomes de carbone et s = 0, ou bien dans laquelle B représente un groupe alkylène comportant 2 atomes de carbone et r = 0, et

où m, o, p, q sont des valeurs numériques représentant la molarité des motifs constitutifs A, B, C et D présents dans les polymères, en proportion de

m:o:p:q = (0,05-0,9):(0,1-0,95):(0-(<0,3)):(0-(<0,3)), et où

p + q < 0,3,

de telle sorte que m + o + p + q = 1.

9. Polymère acrylique modifié selon la revendication 8, dans lequel 50 - 100% molaires de la formule C sont repré-

sentés par une structure dans laquelle A représente un groupe alkylène comportant 2 atomes de carbone et $u = 0$ ou dans laquelle B représente un groupe alkylène comportant 2 atomes de carbone et $t = 0$.

10. Polymère acrylique modifié selon la revendication 8 ou 9, dans lequel $p + q \neq 0$.

11. Polymère acrylique modifié selon l'une quelconque des revendications 8 à 10, dans lequel $m:o:p:q = (0,05-0,9):(0,1-0,95):(0-(<0,1)):(0-(<0,1))$ et dans lequel $p + q < 0,1$.

12. Polymère acrylique modifié selon l'une quelconque des revendications 8 à 10, dans lequel $m:o:p:q = (0,05-0,9):(0,1-0,95):(0-(<0,02)):(0-(<0,02))$ et dans lequel $p + q < 0,02$.

13. Polymère acrylique modifié selon l'une quelconque des revendications 8 à 10, dans lequel $m:o:p:q = (0,05-0,9):(0,1-0,95):(0-(<0,01)):(0-(<0,01))$ et dans lequel $p + q < 0,01$.

14. Polymère acrylique modifié selon l'une quelconque des revendications 8 à 13, dans lequel la limite inférieure de $p + q$ est d'environ 0,001.

15. Polymère acrylique modifié selon les revendications 8 à 14, caractérisé en ce que le poids moléculaire moyen en nombre est de 4 000 à 100 000.

16. Polymère acrylique modifié selon les revendications 8 à 14, caractérisé en ce qu'il peut être obtenu par une synthèse dans laquelle le réactif A-1 présente un poids moléculaire moyen en nombre de 1 000 à 10 000.

17. Polymère acrylique modifié selon les revendications 8 à 16, caractérisé en ce qu'il peut être obtenu par une synthèse dans laquelle le réactif B-1 présente un poids moléculaire moyen en nombre de 250 à 10 000 et le réactif C-1 présente un poids moléculaire moyen en nombre de 250 à 10 000.

18. Polymère acrylique modifié selon les revendications 8 à 17, caractérisé en ce qu'il peut être obtenu par réaction des réactifs A-1 et B-1 et éventuellement de C-1 et éventuellement de D-1 en présence d'un catalyseur acide.

19. Polymère acrylique modifié selon les revendications 8 à 17, caractérisé en ce qu'il peut être obtenu par une synthèse réalisée à l'aide de solvants organiques inertes comme véhicules.

20. Polymère acrylique modifié selon les revendications 8 à 19, pouvant être obtenu en utilisant les réactifs A-1 et B-1, et éventuellement C-1 et éventuellement D-1, où la réaction a été arrêtée à une forte pente de la baisse de l'indice d'acide en fonction du temps, pour donner un polymère à réduction d'eau initiale élevée de plus de 20% et à affaissement décroissant en fonction du temps, qui peut en particulier être utilisé dans des applications de préfabrication.

21. Polymère acrylique modifié selon les revendications 8 à 19, pouvant être obtenu en utilisant les réactifs A-1 et B-1, et éventuellement C-1 et/ou D-1, où la réaction a été arrêtée à une pente moyenne de la baisse de l'indice d'acide en fonction du temps, pour donner un polymère à réduction d'eau initiale élevée ou moyenne d'au moins 10% et à affaissement constant en fonction du temps, qui peut en particulier être utilisé dans des applications de béton prêt à l'emploi.

22. Polymère acrylique modifié selon les revendications 8 à 19, pouvant être obtenu en utilisant les réactifs A-1 et B-1, et éventuellement C-1 et/ou D-1, où la réaction a été arrêtée à une faible pente de la baisse de l'indice d'acide en fonction du temps jusqu'au comportement linéaire, pour donner un polymère à réduction d'eau initiale moyenne ou faible d'au plus 20% et à affaissement croissant en fonction du temps, qui peut en particulier être utilisé dans des applications d'augmentation de l'affaissement.

23. Mélange sous forme solide ou liquide comprenant au moins un polymère acrylique modifié selon les revendications 8 à 22.

24. Mélange sous forme solide ou liquide comprenant au moins un polymère acrylique modifié selon les revendications 20 à 22.

25. Mélange selon la revendication 23 ou 24, caractérisé en ce qu'il comprend au moins deux polymères acryliques

modifiés en proportions diverses, donnant un mélange à haute réduction d'eau et à affaissement constant en fonction du temps.

5 26. Mélange selon l'une quelconque des revendications 23 à 25 comprenant en outre d'autres agents dispersants choisis dans le groupe formé par des condensats de mélamine sulfonée, des condensats de naphthalène sulfoné, des lignosulfonates, des copolymères maléamide/vinyle substitués et des copolymères acryliques ou méthacryliques avec des chaînes latérales polyalkylène glycol, et leurs mélanges.

10 27. Mortier, béton, ciment ou liant pour ciment, contenant au moins un polymère acrylique modifié selon les revendications 8 à 22 en quantité de 0,01 à 10% en poids du liant, ledit mortier ou béton présentant une teneur en unités de composition de liant de 100 à 800 kg/m³, ladite composition de liant étant choisie dans le groupe formé par un ciment, une pâte de ciment, une poudre hydraulique latente, un mélange de poudres hydrauliques latentes, et leurs mélanges, éventuellement avec une ou plusieurs poudre(s) microscopique(s) inerte(s).

15 28. Mortier, béton, ciment ou liant pour ciment selon la revendication 27, **caractérisé en ce que** le ciment est choisi dans le groupe formé par du ciment Portland, du ciment blanc, du ciment alumineux, du ciment Portland avec constituants secondaires, et leurs mélanges, et où la poudre hydraulique latente ou microscopique inerte est choisie dans le groupe formé par de la cendre volante, du laitier, des pouzzolanes naturelles, de la fumée de silice, du schiste bitumineux brûlé, du carbonate de calcium métakaolin, et leurs mélanges.

20 29. Mortier, béton, ciment ou liant pour ciment selon la revendication 27 ou 28, **caractérisé en ce que** le mélange sous forme de liquide ou de poudre contenant les polymères acryliques modifiés est ajouté avant, pendant ou après l'opération de broyage du ciment ou du liant pour ciment.

25 30. Coulis aqueux de poudre microscopique contenant un polymère acrylique modifié selon les revendications 8 à 22, ou un mélange de ceux-ci, en quantité de 0,01 à 10% en poids du liant.

30 31. Coulis aqueux de poudre microscopique selon la revendication 30, **caractérisé en ce que** la poudre microscopique est du carbonate de calcium, du gypse ou est à base de gypse.

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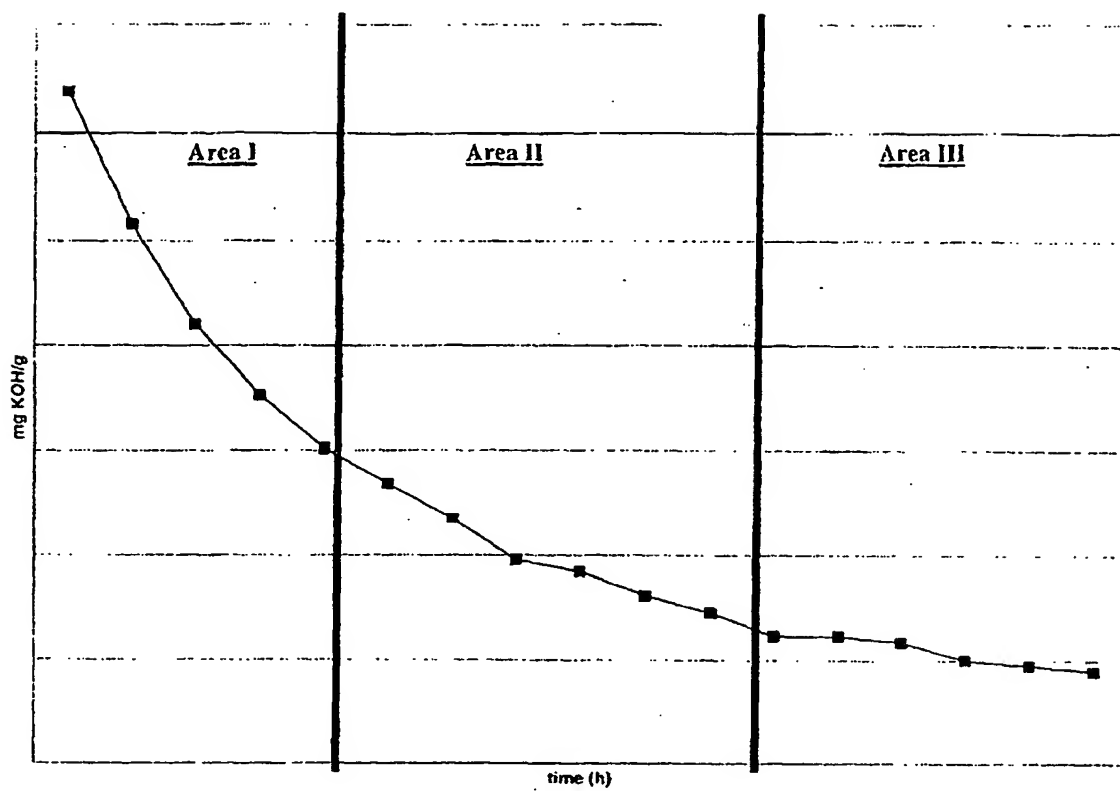


Figure 1

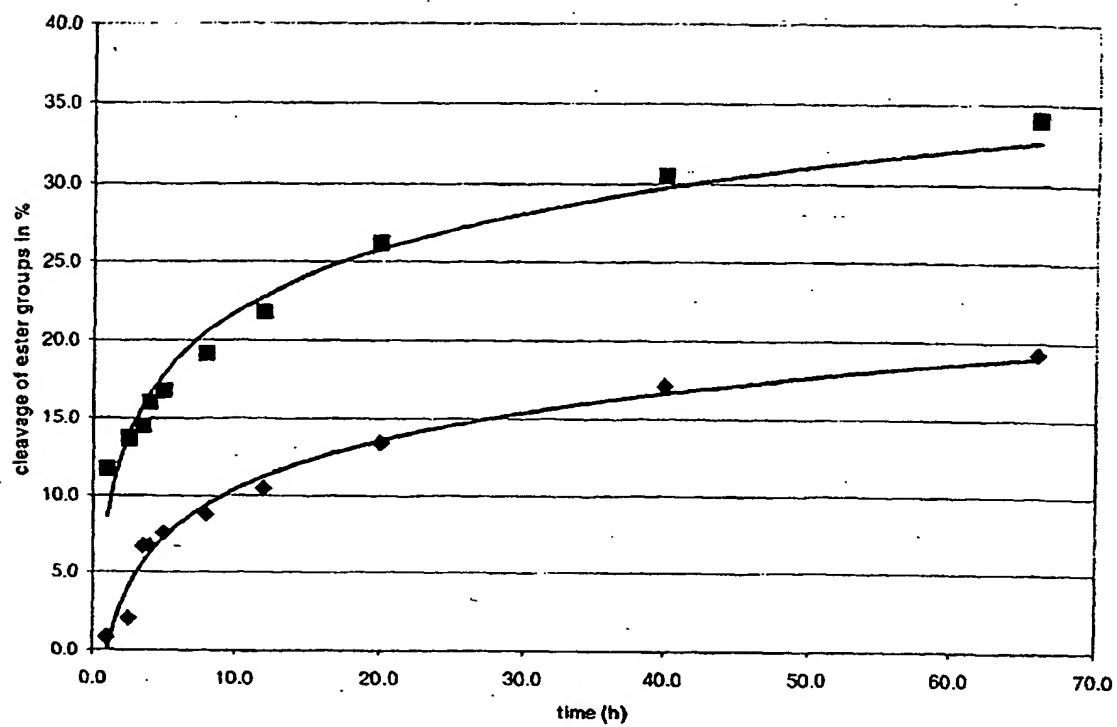


Figure 2